# Production Experience and Performance Characterization of a Novel Immersion Silver

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#### Abstract

Following previous reports by the authors on the general properties of a novel immersion silver process, this paper presents the production experience in typical horizontal lines to demonstrate its robustness. In addition, several reliability issues known to common immersion silver process are discussed; including galvanic attack, solder joint strength and BGA solder joint integrity. It is found that galvanic attack is not necessarily caused by solder mask undercut, but is directly related to silver thickness. The shear strength at the interface of both SnPb and SAC 305 alloy is independent of the silver thickness (0.05 to  $0.5 \mu m$ ) and of Pb-free reflow treatment (up to three cycles). No "planar" micro voids that are detrimental to strength and reliability are found in the BGA solder joints.

#### Introduction

To meet the emerging requirement of eliminating lead from electronics, the printed wiring board (PWB) industry is migrating from hot-air-leveled solder (SnPb) to alternative final finishes, including immersion silver, immersion tin, electroless nickel/immersion gold and organic solderability preservative (OSP) [1]. Among them, immersion silver is considered the leading candidate because of its excellent properties and reasonable cost. The general properties of a novel immersion silver process have already been presented [2,3]. This paper focuses on the production experience in typical horizontal lines to demonstrate its robustness, and several reliability issues known to common immersion process, such as "galvanic" attack of fine copper trace, solder joint strength and BGA integrity.

#### **Experiments**

The robustness of the process was evaluated by monitoring production of printed wiring boards in a horizontal line with process steps shown in Table 1. The pretreatment of cleaning and micro etch is critical to the appearance of the silver coating. The total etch depth was about one to two microns, depending on the quality of incoming copper substrate.

Steps	Application	Temperature, °C	Time, min	
Clean	Spray	30	1-2	
Rinse	Spray	Room temp	1-2	
Micro etch	Flood Immersion	30	1-2	
Rinse	Spray	Room temp	1-2	
Pre-dip	Flood Immersion	40	0.5-1	
Silver	Flood Immersion	50	2-4	
DI Rinse	Spray	Room temp	1-2	
Dry	Hot air	80	1-2	

Table 1 - Typical Steps for Immersion Silver Process

The propensity for "galvanic" attack of the copper trace was evaluated by plating test boards in a commercial horizontal line. First the test boards were processed at the normal line speed of 1 m/min for a dwell time of 2.5 minutes and a silver thickness of 0.25  $\mu$ m (measured on 1.9 mm x 1.9 mm size pad). Next, the test boards were processed under identical conditions up to pre-dip, but the speed in the silver tank was reduced to 0.5 m/min for a dwell time of 5 minutes and a silver thickness of 0.48  $\mu$ m. The copper trace was examined, before and after stripping off the solder mask, by SEM for signs of attack.

The solder joint strength was measured by a shear test. Test boards of BGA pads (0.5 mm diameter) were coated with silver of 0.05, 0.2 and 0.5  $\mu$ m thickness and subjected to three Pb-free reflow cycles with peak temperature of 262 °C. Solder balls composed of Sn63Pb37 and SAC 305 alloys (0.76 mm diameter) were soldered onto the pads with matching solder pastes. The solder ball was sheared off at 200  $\mu$ m/sec by using a Dage PC-4000 Bond Tester as shown in Figure 1.



Figure 1 - Schematic Diagram of the Shear Test

The solder joint integrity of BGA pads was examined by X-rays using a Nicolet Imaging System X160L at 55 kV and 30  $\mu$ A. Using the highly penetrating, non-destructive properties of X-rays, the system creates an image on a video monitor for viewing the internal construction of an object. From examining the image, one can determine if there are hidden defects or internal irregularities in the object, i.e., the percentage of voids in solder joints between components and a PWB. The samples were also examined by cross section for comparison.

## **Results and Discussion**

#### **Production Experience**

As an example, the production of PWBs through one full cycle of bath life was monitored. For a period of nine weeks, a total panel surface area of 12,200 m<sup>2</sup> was processed in a silver tank of 700 liters, a throughput of 17.5 m<sup>2</sup>/L. It included 7000 m<sup>2</sup> of "thick" silver (0.225  $\mu$ m to 0.3  $\mu$ m) and 5,200 m<sup>2</sup> of "thin" silver (0.15  $\mu$ m to 0.2  $\mu$ m). The average silver thickness was 0.203  $\mu$ m on a 2 mm x 2 mm size pad. At the beginning and the end of bath life, the coating was tested extensively for thickness, appearance, adhesion, galvanic attack, tarnish resistance to IR reflow (260 °C/twice), tarnish resistance to aging in humidity (85 °C/85% RH for 12 hours), tarnish resistance to dry baking (155 °C for 4 hours) and solderability. Daily quality control over the entire bath life showed consistent performance in solderability, tarnish resistance after dry baking, and ionic contamination.

The immersion silver process is based on the displacement reaction between the silver ion in solution and the copper metal on PWB. Since the deposition rate is controlled by the reduction of silver ions [2], it increases with silver ion concentration, solution agitation, and temperature. PWBs with different specifications of silver thickness can be easily obtained by changing line speed (i.e., dwell time in the silver tank) and bath temperature. As a result of this displacement reaction, the silver ion needs to be replenished continuously and the copper ion gradually builds up in the silver bath. Therefore, one of the factors affecting the bath life would be its copper loading capacity.

As shown in Figure 2, the amount of silver addition increases linearly with throughput. On average, 0.53 gram of silver is consumed to coat one square meter of PWB, i.e., a slope of 0.53 g/m<sup>2</sup>. With the average silver thickness of 0.203  $\mu$ m, it is calculated that 13% of the PWB surface is copper and coated with silver. Based on the displacement reaction, the "theoretical" rate for copper build up is 0.156 g/m<sup>2</sup>, as indicated by the dotted line. However, it can be seen that the actual copper build up deviates from the "theoretical" rate, and gradually reaches a plateau at 1.6 g/L. This is because the copper is continuously being dragged out of the silver bath by the PWBs. As the concentration increases, the drag out eventually equals the amount generated by the displacement reaction. Thus, a copper loading capacity of 2 g/L is sufficient to handle normal production.

One unique phenomenon of immersion silver is that the thickness decreases as pad size increases. Therefore, IPC-4553 specifies the silver thickness as measured on 1.5 mm x 1.5 mm size pads [4]. As shown in Figure 3, the average thickness gradually decreases from 0.23  $\mu$ m to 0.16  $\mu$ m as the pad area increases from 1 mm<sup>2</sup> (1 mm x 1 mm size pad) to 25 mm<sup>2</sup> (5 mm x 5 mm size pad). The variation of 30% is less than what commonly observed in immersion silver processes and ensures the performance of large pads once the thickness requirement is met on the specified small pad.



Figure 2 - Silver Consumption and Copper Build Up Based on Throughput

#### **Galvanic Attack**

The mechanism of "galvanic" attack of copper trace is similar to that of "crevice" corrosion [5]. Under the normal condition, the copper serves as an anode as well as a cathode, on which the oxidation of copper and the reduction of silver ions take place randomly, resulting in a uniform deposit of silver. However, if a "crevice" is developed between the solder mask and the copper trace, the supply of silver ions inside the crevice is limited, and the copper underneath the solder mask becomes a sacrificial anode, providing electrons to the reduction of silver ions that continues on the exposed area of copper, as shown in Figure 4. Since the amount of electrons needed is proportional to the amount of silver ions being reduced, the severity of galvanic attack increases with exposed copper surface area and silver thickness.



Figure 3 - The Effect of Pad Size on Silver Thickness

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Figure 4 - Schematic Diagram of "Galvanic" Attack of Copper Trace

The degree of galvanic attack under normal production conditions, i.e., 2.5 minutes dwell for 0.25  $\mu$ m, is shown by the SEM photomicrographs in Figure 5. Before the solder mask was stripped off, it can be seen that the copper pads are completely covered with silver, even underneath the overhang of the solder mask above the copper traces. After the solder mask was stripped off, there is no attack of copper found on the left and middle samples, but minor attack on the sample at right. It is important to note that the attack is not underneath the solder mask undercut, but is at the area inside the solder mask/copper interface. When the dwell time was intentionally doubled to 5 minutes to produce an excessively thick silver of 0.48  $\mu$ m, the galvanic attack was more severe. As shown in Figure 6, a groove of about 20  $\mu$ m wide and 10  $\mu$ m deep was formed in and around the copper trace underneath the solder mask.



Figure 5 - Minimal Galvanic Attack to Copper Traces under Normal Production Conditions



Figure 6 - Moderate Galvanic Attack with Excessively Thick Silver

Therefore, the risk of galvanic attack can be prevented or minimized by the following approaches: (1) select a silver process that is less aggressive (i.e., a mild pH) and does not require a thick silver for tarnish resistance; (2) control the micro etch to recommended etch rate; (3) avoid large copper land and fine trace combination in design; and (4) improve solder mask adhesion by optimizing pretreatment, imaging, curing and developing processes, and use of chemical-resistant solder masks. **Solder Joint Strength** 

Figure 7 shows the shear test results for SAC 305 solder. It can be seen that the shear force increases rapidly and linearly up to about 8 N, then gradually reaches a maximum at 10 to 12 N, and decreases until the ball was sheared off. The maximum is viewed as the solder joint strength. It appears that the solder joint strength of SAC 305 is independent of the silver thickness (0.05 to 0.5  $\mu$ m) and reflow treatment. Since the strength depends on the cross sectional area where the shear takes place, the results would vary with the geometrical shape of the solder ball and the clearance between the shear and pad, see Figure 1. EDS analysis of the fractured surface on the PWB side, Figure 8, shows only a trace amount of copper from the copper (0.5%) in the SAC 305 alloy. This confirms that the fracture occurred within the SAC alloy (cohesive failure), not at the solder/copper interface (adhesive failure), and that the actual shear force at the solder/copper interface is greater than the shear strength of the SAC 305 solder.

The corresponding results for SnPb solder are shown in Figures 9 and 10. Again, the shear strength is independent of the silver thickness and reflow treatment, and the fracture occurred with the SnPb solder.



Figure 7 - Shear Curve of SAC Alloy on Silver with 0 and 3 Reflows



Figure 8 - SEM and EDS Analysis of the Fractured Surface of SAC 305 Alloy



Figure 9 - Shear Curve of SnPb Alloy on Silver with 0 and 3 Reflows



Figure 10 - SEM and EDS Analysis of the Fractured Surface of SnPb Alloy

## **BGA Integrity**

The BGA investigated in this study was a 26 x 26 array. Five 4x4 arrays from the four corners and center of each BGA were examined by 2D X-ray. As an example, Figure 11 is the X-Ray image of one corner in BGA #2 where a small void, 1.78 area%, can be seen at pad 2. The statistics of 320 pads from the four BGA are summarized in Table 2. The average void size is only 0.62 area%. Since the image cannot tell where the voids are inside the solder and the X-rays system may not be sensitive enough to pick up small voids, the samples were further examined by cross section.

	BGA #1	BGA #2	BGA#3	BGA #4	Total
Number of Pad Checked	80	80	80	80	320
Number of Pad with Void	0	1	4	6	11
Freq. of Pad with Void, %	0.00	1.25	5.00	7.50	3.44
Max. Void Size, area%	0	1.78	0.75	0.60	1.78
Average Void Size, area%	0	1.78	0.57	0.47	0.62





Figure 11 - X-ray Imaging Showing a Void on Pad 2 of BGA



Figure 12 - Cross Section of a BGA and the IMC at Solder/Copper Interface

Figure 12 is the cross section of a BGA solder joint with a known void from X-Ray image. It can be seen that the void is on the component side and is a typical "macro", or "process" void, generated by the evolution of volatile ingredients of the fluxes within the solder paste. At the solder/copper interface there is a layer of intermetallic compound of 3 to 5  $\mu$ m thickness without any sign of "planar" microvoids that are detrimental to the solder joint reliability [6,7]. Thus, with proper process conditions, a BGA solder joint with integrity is formed on immersion silver. It has been reported that the organic content in the silver coating is one of the contributing factor in causing the "planar" microvoids [8,9]. Therefore, the low organic content in this novel immersion silver coating [2,3] inherently presents a lower risk for the "planar" microvoids.

## Conclusion

- 1. The new immersion silver process provides a production proven, high quality PWB finish with a high throughput capacity.
- 2. The degree of "galvanic" attack is directly related to silver thickness, not necessarily caused by solder mask undercut.
- 3. The shear strength at the copper/solder interface is greater than that of the SnPb and SAC solders, and is independent of the silver thickness and Pb-free reflow treatment.
- 4. BGA solder joints are free of "planar" microvoids that are detrimental to strength and reliability.

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